FABRICATION OF 316L STAINLESS STEEL (SS316L) FOAM VIA POWDER COMPACTION METHOD

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ABSTRACT

Metal foam is the cellular structures that made from metal and have pores in their structures. Metal foam also known as the porous metals, which express that the structure has a large volume of porosities with the value of up to 0.98 or 0.99. Porous 316L stainless steel was fabricated by powder metallurgy route with the composition of the SS316L metal powder as metallic material, polyethylene glycol (PEG) and Carbamide as the space holder with the composition of 95, 90, 85, 80, and 75 of weight percent (wt. %). The powders were mixed in a ball mill at 60 rpm for 10 minutes and the mixtures were put into the mold for the pressing. The samples were uniaxially pressed at 3 tons and heat treated by using box furnace at different sintering temperature which are 870°C, 920°C, and 970°C separately. The suitable sintering temperature was obtained from the Thermal Gravimetric Analysis (TGA). There are several tests that have been conducted in order to characterize the physical properties of metal foam such as density and porosity testing, and the morphological testing (Scanning Electron Microscopy (SEM)), and Energy Dispersive X-ray (EDX). From the result, it can be conclude that, the sintering temperature of 920°C was compatible temperature in order to produce the metal foams which have large pores. Other than that, the composition of 85 and 75 wt. % is the best compositions in order to creates the homogenous mixture and allow the formation of large pore uniformly compared to other compositions which in line with the objective to produce foams with low density and high porosity which suitable for implant applications. The average pore size was within range 38.555µm to 54.498 µm which can be classified as micro pores.

ABSTRAK

Logam berbusa adalah struktur sel yang diperbuat daripada logam dan mengandungi liang-liang di dalam strukturnya. Logam berbusa yang juga dikenali sebagai logam berliang yang mempunyai sejumlah besar keporosan pada strukturnya dengan nilai sehingga 0.98 atau 0.99. Struktur berliang 316L keluli tahan karat telah difabrikasi dengan kaedah metalurgi serbuk dengan komposisi serbuk logam SS316L sebagai bahan logam, Polyethylene Glycol (PEG) sebagai penguat dan Baja Urea sebagai pemegang ruang dengan komposisi bahan 95, 90, 85, 80, dan 75 peratus berat (wt. %). Kesemua serbuk dicampur dan diadun menggunakan pengisar bebola pada kelajuan 60 rpm dalam masa 10 minit dan campuran dimasukkan ke acuan untuk ke proses penekanan. Sampel dipadatkan dengan tekanan 3 tan dan di sinter menggunakan relau kotak pada suhu yang berbeza iaitu 870°C, 920°C, dan 970°C secara berasingan. Suhu sinter yang sesuai diperolehi daripada Analisis Gravimetrik Haba (TGA). Terdapat beberapa ujikaji dijalankan untuk mencirikan sifat fizikal logam berbusa seperti ujikaji ketumpatan dan keliangan, ujikaji morfologi dengan menggunakan Pengimbas Mikroskopi Elektron (SEM) dan Tenaga Serakan Sinar-X. Daripada keputusan, dapat dirumuskan suhu sintering 920°C adalah paling sesuai untuk digunakan untuk menghasilkan sampel dengan saiz liang yang besar. Selain itu komposisi 85 dan 75 wt. % adalah komposisi terbaik, di mana komposisi ini menghasilkan campuran yang homogen yang membenarkan pembentukan liang yang besar secara seragam di mana selaras dengan objektif asal kajian untuk menghasilkan logam berbusa yang mempunyai ketumpatan yang rendah dan keliangan yang tinggi di mana sesuai untuk aplikasi implan. Purata saiz liang adalah dalam julat 38.555µm hingga 54.498µm dan boleh diklasifikasikan sebagai liang mikro.

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INTRODUCTION

1.1 Background of Study

At present, high requirement of lightweight constituent make metal foams extremely attractive as an industrial technology for biomedical application which is demanding on weight reduction (Gauthier, 2008). The physicality of metal foam is high porosity make metal foams very lightweight. Basically, metal foams are artificial porous medium that has solid matrix structure of metal consist of empty or fluid-filled voids. Metal foams have been characterized into two types which are open-cell and closed-cell. The foams is called open-cell when the voids are connected via open pores, but when the foams are separated by the solid walls and not connected via open channel are described as closed-cell (Dukhan, 2013).

In order to achieve the metal foams which suitable in orthopedic application and have good properties such as low density, high strength-to-weight ratio, excellent mechanical properties, biocompatibility and corrosion resistance, the suitable materials have to choose carefully. Metals are the most suitable material to fabricate the metals foam proportionate to the ceramic and polymer. Even though the ceramic material have excellent corrosion resistance but ceramic cannot being employed as load bearing implants due to their brittle properties, whereas polymeric systems cannot sustain the mechanical forces present in joint replacement surgery (Ryan, Pandit & Apatsidis, 2006). There are various types of metal that have been used as main materials to fabricated metal foams includes titanium, titanium alloys, nickel, aluminum, magnesium, and stainless steel(Rosip *et al.*, 2013).

Since early 1960s, Stainless steel widely used in orthopedic application such as fabrication of femoral stems, balls and acetabular cups, fabrication of knee and femoral components and tibial trays because of its biocompatibility and inexpensive (Davis, 2003). Porous Stainless steel is compatible to use as a coating on Stainless steel implants. The methods that use to fabricate these coating are by sintering beads or thermal spray techniques. The oxides that formed on the surfaces of stainless steel is more stable than the oxides formed if using titanium and titanium alloys and leads to the crevice corrosion and degradation of the implants. Because of that, Stainless steel is choosing to replace other materials over the year. Stainless steel has been approved in terms of mechanical properties and clinical trials by the US Food and Drug Administration (FDA). Its mechanical properties are often used as bench mark criteria to evaluate other alloys for stent applications (Chen *et al.*, 2014).

There are large varieties of fabrication techniques for metal foams or similar porous structures but usually favorable technique is liquid phase or powder metallurgy process. By using compaction method, metal powders are mixed with foaming agent and then compacted by using hot pressing, cold pressing, hot extrusion, or co-extrusion. The final product of the compaction process is a dense foamable material that can be worked into sheets and profiles (Banhart & Baumeister, 1998) Slurry method are commonly used to produce metal foams by providing metal powder, blowing agent and a binder that mix together and the mixture poured into mould and left to the elevated temperature until melting temperature(Rosip *et al.*, 2013). Casting process also has been used to produce metal foams around inorganic hollow spheres with a liquid melt or using open porosity polymer foams as starting points.

This research is to fabricate the 316L Stainless Steel (SS316L) foam prepared by Compaction technique and to study and characterize the properties of SS316L foam after sintering process. The SS316L have used as a raw material and Polyethylene glycol (PEG) and Carbamide are used as a binder and space holder respectively. The material will be mixed by using ball milling machine to get the homogenous mixture. After that the compaction process will be held by using conventional axial pressing. This process is known as powder metallurgy technique. The Properties Characterization will be measured by doing density and porosity test, Thermal Gravimetric Analysis (TGA), Scanning Electron Microscopy (SEM), and Energy Diffraction X-ray (EDX).

1.2 Problem Statement

The major challenges that need to focused while producing metal foam is the mismatch of the properties between bones and the metallic material. Due to this mechanical mismatch, bone is insufficiently loaded and become stress shielded, which eventually leads to bone resorption (Ryan et al., 2006).

Thus, there are factors need to be considered includes the interconnecting pores that suitable with bone, the pores of the implants same with the pores of bone, the shape and the density of implants is same with the shape and density of bones.

1.3 Objectives

The objectives of this research are:

i) To fabricate the 316L Stainless Steel (SS316L) as metallic cell prepared by Compaction technique.

ii) To characterize the properties of fabricated SS316L foam after sintering process.

1.4 Scope of Study

The scope of this research includes:

i) The percentage of the composition for the SS316L powder are 95, 90, 85, 80 and 75 of weight percent (wt. %) respectively, for the Polyethylene glycol is 1 of weight percent (wt. %) and balance is for the Carbamide composition.

ii) The sintering temperatures that have been choosing are 870^{O}C, 920^{O}C, and 970^{O}C.

iii) The characterization for the properties of metal foam will be study by conducted the Thermal Gravimetric Analysis (TGA), Density and porosity test, Scanning Electron Microscopy (SEM), and Energy Diffraction X-ray (EDX).

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

This chapter justify about literature review of the research to gather information and knowledge of the material that need to be used in this research, the method that have been used in previously study and the method that has been select in this research. This section focused on the Stainless Steels and its properties, the binder and space holder that has been used and the fabrication method that involved.

2.1.1 Metal Foam

Basically, metal foam can be described as the cellular structure that made from metal and have pores in their structures. Metal foam also known as the porous metals, which express that the structure has a large volume of porosities with the value of up to 0.98 or 0.99. The high porosity contributes lightweight to the metal foams. Besides, the terms foamed metal or metallic foam illustrate the fabrication or forming process of the metal foam.

Metal foams have been characterized into two types of structure which are open cell and closed cell. The structure of the porous metals influences the applications of the metal foams. Closed cell foam can be described as the pores is fill with gas and separated from each other by metal cell walls, have good strength and usually used in structural application. Open cell foam contain a continuous network of metallic struts and the enclosed pores in each strut frame are connected, the strength are weaker than the closed cell and are mainly used in functional applications where the continuous nature of the porosity is exploited (Kennedy, 2012). Figure 2.1 show the example of the microstructure of closed cell foam and open cell foam for metal foams.

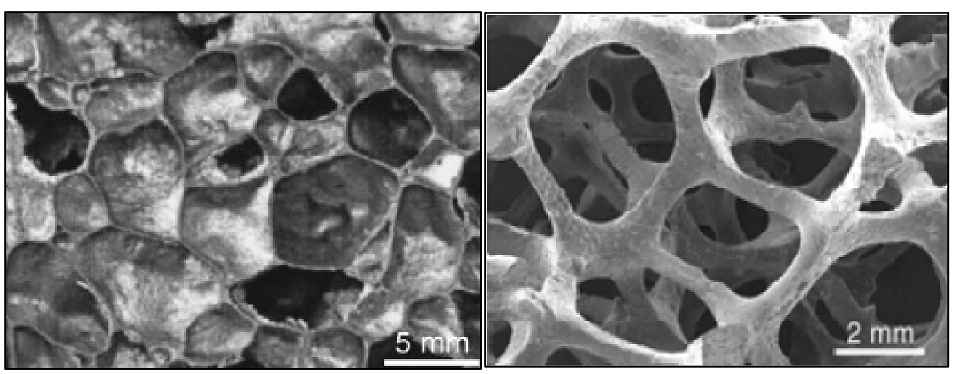

Figure 2.1: Microstucture of (left) a closed cell foam and (right) an open cell foam (Kennedy, 2012)

There are other application of metal foams such as energy absorber, heat exchangers, mechanical damping and in filters system. Nowadays, metal foams has been use in biomedical application as bone implants. Metal foams have excellent potential for implant application due to its low density and good combination of properties because of the reduced stiffness mismatches. Other than that, it is important to make sure the bone ingrowth which possible by metal foams and greatly improve the bone implant interface and may allow for efficient soft tissue attachment supplementing the stability of the implant by biological fixatation (Mariotto *et al.*, 2011).

2.2 Metallic Material

The excellent of electrical and thermal conductivity and mechanical properties make metal used as biomaterials which suitable used as biomedical materials. Biomaterial can be expressed as any material used to make devices to replace a part or a function of body in a safe, reliable, economic, and physiologically acceptable manner (Park & Lakes, 2007). Metals offer excellent strength and resistance to fracture, which suitable for the medical application that requiring load bearing.

There are number of metallic material that good biocompatibility which are not cause serious toxic reaction in human body such as Stainless Steels, Cobalt Alloys, Titanium Alloys and noble metals. These metals are suitable for the structural application in the body such for implants for hip, knee, ankle, shoulder, wrist, finger, or toe joints. These metals have the ability to bear significant loads, withstands fatigue loading, and undergo plastic deformation prior to failure, made these metals are popular chosen as material for the implant application (Shi, 2006).

Some metals have high corrosion resistances which made its suitable used as passive substitutes for fracture healing aids as bone plates and screws, spinal fixation devices, and dental implants. Corrosion can be defined as the unwanted chemical reaction of a metal with its environment, resulting in its continued degradation to oxides, hydroxides, or other compound. It is important to choose metallic materials which have high corrosion resistance due to its biocompatibility in human body.

Other than that, metallic material play active roles in devices such as vascular stents, catheter guides wires, orthodontic arch wires, and cochlea implants (Park & Lakes, 2007). Figure 2.2 show the typical implant applications for orthopedic purposes.

During the twentieth century, the first metallic material was successfully used in orthopedic applications were Stainless Steels and Cobalt-Chrome Based Alloys (Navarro *et al.*, 2008). The Stainless Steels and Cobalt-Chrome Based Alloys have high corrosion resistance based on the presence of Chromium in their properties make it has the ability to render the alloys passive. In this research, the metallic material that has been used is Stainless Steels which will be explained later.

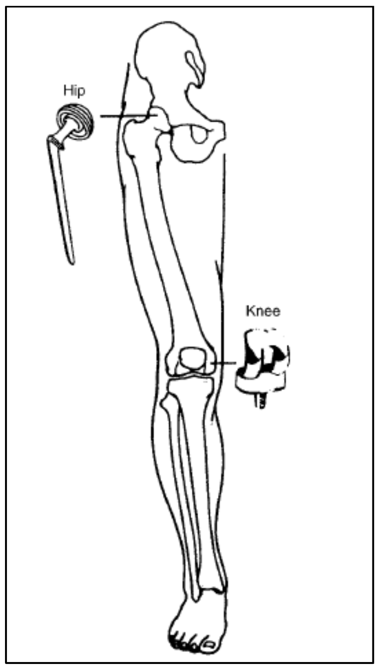

Figure 2.2: The typical implant applications for orthopedic purposes (Davis, 2003)

2.2.1 Stainless Steels

Stainless Steels are widely used in modern metallurgy. Historically, Stainless Steel was discovered in early 18th and 19th centuries; when the identification of Chromium as an element was begin. Harry Brearley (1871-1940) who first produced the first commercial cast of martensitic Stainless Steel, which used for cutlery area (Cobb, 2010).

Different from other alloy systems that has widely used such as Carbon Steels, Alloy Steels, and Aluminum Alloys, that are relatively dilute solution of several element in the parent matrix. Stainless Steel is one of alloys system that it is not a dilute solution. There are several percent of alloying element that contained in Alloys steels includes Carbon, Manganese, Nickel, Molybdenum, Chromium, and Silicon, Impurities Sulfur, Oxygen, And Phosphorus. Typically, Alloy Steels contain very small of amounts of Titanium, Niobium and Aluminum. In contrast, in about 11% of Chromium that contain alone in Stainless Steel (McGuire, 2008). Usually, the shape of Stainless Steels particles is irregular. Figure 2.3 show the basic shape of metal powder (Kalpakjian & Schimid, 2006).

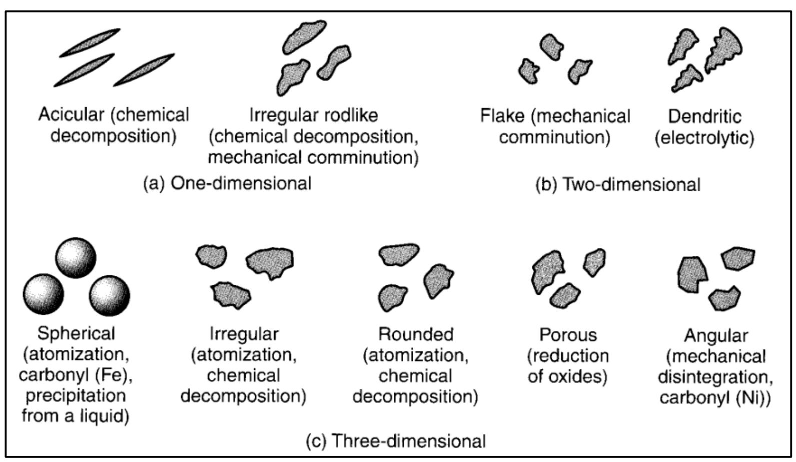

Figure 2.3: Basic shape of Metal powder (Kalpakjian & Schimid, 2006)

Basically, Stainless Steel is Iron-Base Alloys that contain a minimum of approximately 11% of Chromium (Cr), amount that needed to prevent the formation of rust in unpolluted atmosphere. There are few Stainless Steels contain more than 30% Cr or less than 50% Ferum (Fe). They fulfill the Stainless Steel characteristics condition by the formation of an invisible and adherent Chromium rich oxide surface film. The process is happen when the oxide forms and heals itself in the presence of oxygen (Davis, 1994).

There is development of Stainless Steels that used in implant application. The first Stainless Steel that has been recorded that utilize as implant fabrication was the 18-8 type which is stronger and more resistance to corrosion than the Vanadium Steel. There are some improvement has been done to Stainless Steel by attached a small percentage of Molybdenum to improve the corrosion resistance in Chloride solution which next the Stainless Steel has known as type 316 Stainless Steels. During 1950s, they upgrade the Stainless Steel by reducing the amount of Carbon content from 0.08 to a maximum amount of 0.03% to increase corrosion resistance and minimize the sensitization and become as type 316L Stainless Steels. The Chromium content also function as the reduction of Carbon content in which to impart corrosion resistance in Stainless Steel which the concentration of Chromium is 11% (Wong & Bronzino, 2007).

The type of Stainless Steels that most widely used for implant fabrication is the austenitic Stainless Steels which is type 316 and 316L. These groups of steel are nonmagnetic and have better corrosion resistance than others because the content of Molybdenum that enhances the resistance while attach in the salt water. The American Society of Testing and Material (ASTM) recommend type 316L rather than type 316for fabrication for implant. The standard composition of 316L Stainless Steel that follows American Society for Testing and Materials is show in Table 2.1 (Wong & Bronzino, 2007).

Table 2.1: Standard composition of 316L Stainless Steel (Wong & Bronzino, 2007)

Element	**Composition (%)**
Carbon	0.03 max
Manganese	2.00 max
Phosphorus	0.03 max
Sulfur	0.03 max
Silicon	0.75 max
Chromium	17.00-20.00
Nickel	12.00-14.00
Molybdenum	2.00-4.00
Ferum	Balance

Mariotto *et al.,* (2011) in the study of fabrication metal foam for biomedical application have used Stainless Steel type 316L as main material. Ammonium Carbonate and Ammonium Bicarbonate is chosen as foaming agents that will mix with the Steel powder. The technique that has been applied to fabricate the metal foam is by using powder metallurgy techniques and the metal foam vacuum heat treated in 2 stages, the first stage at 200°C for 5 hours to decompose the carbonate and the second stage at 1150°C for 2 hours to sinter the steel. From the research, the density of the metal foam is in about 0.3 g.cm$^{??}$ and 0.5g.cm$^{??}$ for Ammonium Carbonate and Ammonium Bicarbonate foaming agents respectively. The microstructure of the metal foam is heterogeneous pore structures, composed by irregular and isolated pores. The result show that the metal foam produced can be viable in orthopedic implants (Mariotto *et al*., 2011).

The previous researchers produce of 316L Stainless Steels foam via slurry method. In the research, the 316L Stainless Steel is chosen as metallic material, where the Polyethylene Glycol (PEG) and Methylcellulose (CMC) were used as binder. The result shown that, the SS316L metal foams had been successfully produced by using slurry method. The microstructure observation show that the metal foams had closed pore than open pore and the powder particles did not well growth to combine each other after sintering process. At the end of the research, the suitable composition of SS316L for metal foams fabrication is gained with the suitable sintering temperature which resulted better strength of metal foams (Rosip *et* *al.*, 2013). Gauthier (2008) in his study of structure and properties of open-cell 316L Stainless Steels foams produced by a powder metallurgy-based process used type 316L Stainless Steel as main material, a polymeric binder, and chemical foaming agent. All the material was dry mixed, then the mixture was molded and heat treatment is applied to the metal foam. From the result of the investigation, the 316L Stainless Steels foams was produced and the heterogeneous foams feature a mix of open and closed pores depending on processing conditions. The mechanical properties that get from the test show that the value is following the scaling for metal foams and was related to foam density (Gauthier, 2008).

In this research, the 316L Stainless Steels is choosing as main material. The characteristic of the 316L Stainless Steel will be elaborate later in the next topic.

2.2.2 Designation of Stainless Steels

The designation of Stainless Steels can be divided into three different designation systems in principle which are the designation of wrought Stainless Steels, cast Stainless Steels and P/M Stainless Steels. Basically, in United States the American Iron and Steel Institute (AISI) numbering system and the Unified Numbering System (UNS), are design the wrought grades of Stainless Steels. Other major industrial have also been established other designation system of Stainless Steels but it also similar to the AISI. Basically for wrought Stainless Steels, the UNS designation consist of the letter “S”, follow by a five-digit number whereas for those alloys that have an AISI designation, the first three digit of the UNS designation usually correspond to an AISI number. The UNS designation consists of the letter “N” followed by a five-digit number when Stainless Steels that contain high Nickel content (>25 to 35%) (Reardon, 2011).

There are institutions which call as High Alloy Product Group of the Steel Founder’s Society of America, also known as the Alloy Castings Institute (ACI), has designated standard cast Stainless Steels grades. The composition and properties of the Stainless Steels similar to the wrought grades, and some cast Stainless Steels are modified in order to improved cast ability and the higher silicon levels are typically used in cast Stainless Steels for the improvement. The designated of Cast Stainless Steels as alloys intended primarily for liquid corrosion service (C) or high-temperature service (H). The nominal Chromium-Nickel type of the alloy denotes by the second letter of the designation and it will change when the Nickel content increases. The maximum Carbon content (percentage x100) is represented by the numeral or numerals following the first two letters. When there are another alloying element is present, these are indicated by the addition of one or more letter as a suffix. So that, from the Figure 2.4 it can be described that the designation of CF-8M refers to an alloy for corrosion-resistant service (C) of the 19Cr-9Ni type, with the maximum Carbon content 0.08% and containing Molybdenum (M) (Davis, 2000).

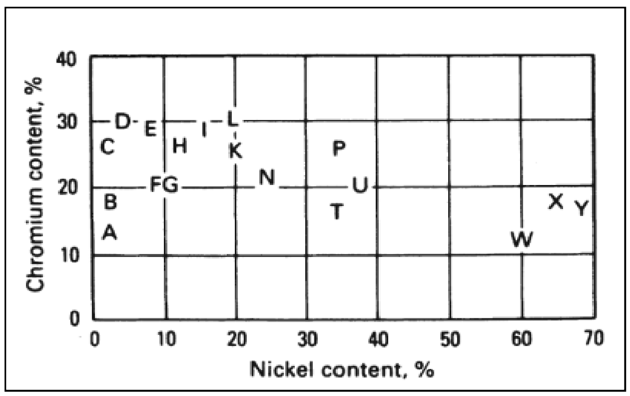

Figure 2.4: Chromium and Nickel contents in ACI standard grades of heat-resistant and corrosion-resistant Stainless Steel castings (Davis, 2000)

The Metal Powder Industries Federation (MPIF) establishing the designation for P/M products. The popular grades of wrought Stainless Steels have been taking as mark of derivation of new composition of P/M Stainless Steels. Because of that, the characteristics of most P/M Stainless Steels are parallel to the wrought Stainless Steels. The wrought Stainless Steels have a maximum of Carbon content of 0.08% or higher but there are few selected of wrought Stainless Steels are available in a low Carbon with maximum Carbon content of 0.03% and these are designated as “L” grades. For the P/M Stainless Steels, with the exception of the martensitic grades, are specified to be “L” grades or the low Carbon of the alloys. There are reasons on why the P/M Stainless Steels need for the low Carbon requirement includes low Carbon content renders the Stainless Steels powder soft and ductile, making it easier to compact, and it minimize the potential for Chromium Carbide formation or being sensitive during cooling from the sintering temperature (Davis, 2000).

2.2.3 Classification of Stainless Steels

The classification of Stainless Steels can be divided into five which are martensitic, ferritic, duplex, and austenitic which based on the characteristic crystallographic structure of the alloys while the fifth is the precipitation-hardenable alloys which based on the type of heat treatment used. Figure 2.5 illustrate the common crystal structure of metal such as body-centered cubic (BCC), face-centered cubic (FCC), and hexagonal close-packed (HCP) (Shi, 2006).

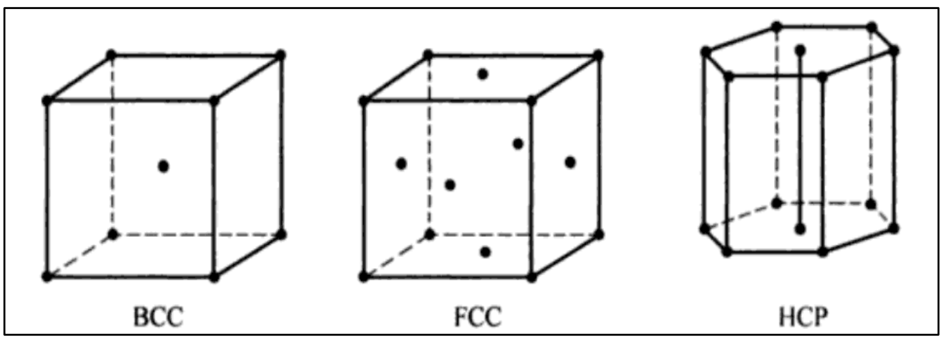

Figure 2.5: The common crystal structure of Metal such as body-centered cubic (BCC), face-centered cubic (FCC), and hexagonal close-packed (HCP) (Shi, 2006)

Martensitic Stainless Steel can be described as Fe-Cr-C alloys that possess body-centered tetragonal crystal structure (martensitic) in the hardened condition. The properties of martensitic Stainless Steel are ferromagnetic, hardenable by heat treatments, and generally resistant to corrosion in mild environments. These types of Stainless Steel have high hardness value make it suitable for dental and surgical instruments. Basically, ferritic Stainless Steel contain Iron-Chromium Alloys with body-centered cubic (bcc) crystal structures. The applications of these types of Stainless Steel are solid handles for instruments, guide pins and fastener. Duplex Stainless Steel is a two phase alloys which have equal proportions of ferrite and austenite phases in their microstructure and characterize by their low carbon content, additions of molybdenum, nitrogen, tungsten, and copper. Different from other types of Stainless Steel that have applications in biomedical, duplex Stainless Steel are commonly used in the oil and gas, petrochemical, pulp and paper industries. The precipitation-hardenable (PH) Stainless Steel is the only type of Stainless Steel that classified by the heat treatment. Basically, these types of Stainless Steel are Chromium-Nickel grades that can be hardened by an aging treatment which can be classified into three categories which are austenitic, semi-austenitic and martensitic. Usually, the precipitation-hardenable (PH) Stainless Steel has applied in medical such as neurosurgical aneurysm and micro vascular clips and various types of surgical and dental instruments (Davis, 2003).

In this research, the type of the Stainless Steels that will be used can be classified as austenitic Stainless steels. Austenitic Stainless steel has largest numbers of alloys and use. Same with the ferritic Stainless steel, the austenitic Stainless Steel cannot be hardened by heat treatment. The other properties for the austenitic Stainless steels are nonmagnetic in the annealed condition and can be hardened only by the cold working. The application for the austenitic Stainless Steel such dental impression trays, guide pins, holloware, and hypodermic needles, sterilizer, and other application that have a complex shape. These type of Stainless Steels also has widely used for implants (Davis, 2003).

2.3 Binder

Binders play an important role in processing of component by using pressing method. Basically binders can be described as multi-component mixtures of several Polymers which consist of some additives that add to the primary component include dispersants, stabilizers, and plasticizers. The function of the binders is to assist in shaping of the component during the process of fabrication to provide strength to the shaped component. Binders also hold the metal particles together until the onset of sintering. The density of a pressing (small pressed part) increases with the use of a binder plasticizer). The binder's properties can influence on the metal particles distribution, shaping process, dimensions of the shaped component, and the final properties of the sintered component. The binder provides strength which can avoided the green body to the formation of defects such as cracking and blistering (Heaney, 2012). The binder will be eliminated from the shaped component during the firing process without any disruptive effect (Angelo & Subramanian, 2008).

There are ideal characteristics that binder should have followed. A good binder that used in shaping must have low inherent viscosity at the shaping temperature, must be strong and rigid after shaping, and should have low molecular weight. When the binder regard to powder interaction, a binder must wet and adhere to the powder, be chemically passive, and be stable during mixing and shaping. After shaping process, the shaped component will be firing and the binders will be burnout. So that, a binder must be noncorrosive and giving nontoxic products on decomposition leave no residue on burnout, have a decomposition temperature above and below mixing temperature. From the context of manufacturing process, a binder that used for shaping must be readily, safe and low cost, have long shelf-life, low water absorption and no volatile components and have high strength and stiffness (Angelo & Subramanian, 2008).

There are investigations of producing the metal foams which contain binder. The previous researchers study the production of micro-porous austenitic Stainless Steels by powder injection moulding route. The material that have been used in order to produce porous structures is 316L Stainless Steel as the main material, a multiple-component binder system consist of Paraffin wax (PW), Polypropylene (PP), Carnauba wax (CW), and Stearic Acid (SA), and spherical Poly(Methyl Methacrylate)(PMMA) particles were used as a space holder material (Gülsoy & German, 2008). Other investigation that produce the metallis foams was the study of fabricating 17-4 PH Stainless Steels foam for biomedical application used Polyvinylalcohol (PVA) as binder which added to the mixture of Stainless Steel and Carbamide to increase the green strength of the sample (Mutlu & Oktay, 2013). Open cell Fe-10% Al Foam was fabricated by using space holder technique by mixing Ferum and Aluminum solution (FeAl) with Natrium Cloride (NaCl) and Polyester resin as space holder and binder respectively in order to study the characterization of the foams (Golabgir *et al.*, 2014).

2.3.1 Polyethylene Glycol (PEG)

Polyethylene Glycol (PEG) is available in molecular weight from 400 to 12000 but low molecular weights are liquids at room temperature. The most compatible molecular weight of PEG is from 6000 to 12000 which are used in most application at higher end. There are many type of PEG such as waxy solids that are soluble in water, Methylene Chloride, and Acetone. PEG is clean chemical that burnout during firing process. PEG has a low strength binder, and it is sufficient for most purpose. Usually, PEG is added as solution or in fluid emulsion condition in order to obtain a homogenous fluid without making a binder clotted (King, 2001). PEG is water-soluble Polymer and frequently used as a binder, plasticizer or a lubricant. PEG binder is about 10 times more pure compared with Polyvinyl Alcohol (PVA) (Watchman, 2009).

There are many series of PEG members that can be categorized by its molecular weight. The average molecular weights of 200 to 20,000 can be categorized as the intermediate members which can be produced by the Sodium or Potassium Hydroxide-Catalyzed batch polymerization of Ethylene Oxide onto water or Monoor Diethylene Glycol. The fabrications of the Polymer are by stepwise anionic addition polymerization and therefore possess a distribution of molecular weights. Usually, the application of this type of PEG is commercial uses for products in metal forming, Ceramic and Rubber –processing operations. The molecular weights from 100,000 to 10,000,000 can be categorized as the highest members of PEG. The fabrication of these members is by using the special anionic polymerization catalysts that incorporate Metals such as Aluminum, Calcium, Zinc, Iron, and coordinated ligands includes Amides, Nitriles, or Ethers. This type of PEG is widely used because of their ability at very low concentration to reduce friction of flowing water (Schwartz, 2002).

The application of PEG can be found in medical and biotechnical because of the range of properties. In medical and biotechnical applications, the needs of amphilicity behavior make PEG has widely used because of these Polymers of Ethylene Oxide can be described as amphiphilic which can soluble both in water and in most organic solvents. Other than that, PEG also can be found in Ceramic applications which used as components of Ceramic slips and glazes for the manufacture of Porcelain signs and other Vitreous coatings (Schwartz, 2002). Other application of PEG is as a binder in manufacturing for shaping components such as can be used in injection molding process, casting, extrusion, and powder compaction. Figure 2.6 show the PEG that will be used in this study.

There are previous researchers that use PEG as binder such as the investigation of fabrication of 316L Stainless Steels foam by using slurry method used binder such PEG and Methylcellulose (CMC) (Rosip *et al.*, 2013). There are other researchers that used the same method of fabrication in order to investigate the influence of composition and sintering temperature on density for pure and Titanium Alloy foams. The Titanium slurry was prepared by mixing pure Titanium and Titanium Alloys powder with PEG as a binder to fabricate the foams (Ahmad *et al.*, 2010). Rafter et al. in her study of development of SS316L foams with different composition using compaction method use PEG as binder that mixed with SS316L powder and crystalline Sugar as space holder (Rafter *et al.*, 2014).

Figure 2.6: Polyethylene Glycol (PEG)

2.4 Space Holder

The terms Space holder play important role in order to produce metal foams. It is important to make sure the suitable space holder is selected. The basic characteristics of the space holder is has to be easily removable later by the thermal decomposition either by rinsing it out or by leaching in solvents like water or alcohol. The good criteria of space holder is its can be removed without leaving any residues and any reaction does not occur with the metal powder, which can affect the metal powder if the powder contains highly reactive elements like Titanium or Magnesium (Dukhan, 2013).

The size and shape of space holder also have to carefully select because of the pores are connected to the space holder granules, elongated pores or pore structure and tailored density gradient. When the selection process is finished, the next process is the space holder will be mixed together with specific metal powder and compacted into a desired shape component by conventional techniques such axial pressing or isostatic pressing. The higher force that applied to the compact part during compaction process due to get higher compaction pressure to make the part have strength and the next process can be instituted. It is important to make sure the strength of the compact part is sufficient enough to survive after the space holder will be removed during sintering process (Dukhan, 2013).

There are many different space holder material that widely used includes Polymeric material, Sodium Chloride, Crystalline Sugar Cane, Sodium Fluoride, Carbamide, Ammonium Hydrogen Carbonate, Magnesium and Tapioca Starch (Rafter *et al*., 2014). In this study, the space holder that used is Carbamide or also known as Urea. Basically, the shape of the Carbamide is spherical and it is high solubility in water.

Previous researcher has applied the space holder in the fabrication of metal foams. The research to investigate the compressibility of porous Magnesium foams which fabricated via powder metallurgy method and Carbamide ($CO\ (NH_2)_2$) is choose as space holder particles (Wen *et al*., 2001). Other than that, other researchers study the fabrication porous 316L Stainless Steels with two different space holder which are Ammonium Carbonate and Ammonium Bicarbonate to compare the properties of the metal foams by using powder metallurgy techniques (Mariotto *et al.*, 2011). The pure Titanium and Titanium Alloys foams were fabricated by using the slurry method to produce the metal foams with addition the Polyethylene Glycol as the binder and the Methylcellulose as the space holder. This aim of this investigation was to study the characterization of the pure Titanium and Titanium Alloys foams (Ahmad *et al.*, 2014). The other research that involved binders consumption is the study of powder metallurgy synthesis of Steel foams has use the Steel powder which contain of 2.5% Ferum (Fe) and 0.2% Carbon (C) which are the two materials that had been choose as space holder which are Magnesium Carbonate ($MgCO_3$) and Strontium Carbonate ($SrCO_3$) (Park & Lakes, 2007).

2.4.1 Carbamide (Urea)

The types of space holder that frequently used are Carbamide and Ammonium Hydrogen Carbonate. Carbamide can be removed by treatments at high temperature either before sintering or as an initial step in the sintering heat treatment. Carbamide is used in metal foam fabrication in order to produce porosity for certain higher melting point metals. Carbamide also has been used as space holder for Aluminum and Stainless Steel but it not being removed thermally but by water leaching. Figure 2.7 show the Carbamide particles. The particles of Carbamide have different shapes such as rough spheres or high aspect ratio flakes. The varieties of shape for Carbamide allow the pore shape to be controlled as this shape is preserved in the porous material (Chang & Zhao, 2013).

Figure 2.7: Carbamide particles

There are previous researchers that used Carbamide as the space holder material in fabrication of metallic foam. The high porosity Titanium foam was fabricated by using Carbamide as the space holder material by applying space holder techniques was study by the Kotan & Bor (2007). The Carbamide were dissolved in water before mix with the Titanium powder and compacted by using conventional pressing machine to produce Titanium foams (Kotan & Bor, 2007). The compressibility of porous Magnesium foams which fabricated via powder metallurgy method was studied and the Carbamide (CO $(NH_2)_2$) is choose as space holder particles (Wen *et al.*, 2001). The characterizing of the CR-Si-Ni-Mo Steel foams use CR-Si-Ni-Mo Based Ancorsteel 4300 powders with the Polyvinyl Alcohol (PVA) and Carbamide as binder and space holder material respectively was studied by Mutlu and Oktay (2011).

2.5 Fabrication Techniques

There are various processes that can be classified according to the state of the starting Metal to liquid, powdered, ionized. For liquid Metal, it can be foamed directly by injecting gas, gas-releasing foaming agents or by producing supersaturated Metal gas solutions. Other method that has been used such investment casting and usage of filler materials. Metal foams also can be produced by using Metal powder as starting materials which mix the powder with foaming agents and compacted to a foamable precursor. The Metal slurries techniques also usually used in order to produce Metal foams by using Polymer or powder mixtures (Banhart & Baumeister, 1998).

2.5.1 Metal Foams Fabrication Techniques

The fabrication of Metallic foam was first start by Benjamin Sosnik in year 1948. He produces Metallic foam by creating pores from apply Mercury vapor to molten Aluminum and Mercury. At year 1956, the production of Metallic foam has been done by replacing the Mercury with foaming agents generating gas by thermal decomposition, while during year 1963 there was development of metallic foams by a powder compacting techniques. After the sequence of history of Metallic foams fabrication from the previous researcher, until now, many researcher have developed Metallic foams using the techniques that avoid applying Mercury that caused the toxicity (Chang & Zhao, 2013).

Basically, the fabrication of metal foams can be divided into two categories which are foams made from metallic melts or in the liquid route and foams made from solid metals or can be called as solid state route. In liquid route, it can be described that the porosity can be derived in the form of gas bubbles either by injecting the gas from outside or by inside by decomposed of some chemical such like Titanium Hydride (TiH_2). By contract, in solid state route, the metal powder were used and mixed with other suitable powder or binder which can be removed later by dissolution or decomposition such as firing process (Bhatnagar & Srivatsan, 2009). Figure 2.8 show the four categorizes of metal foams fabrication process (Banhart, 2001).

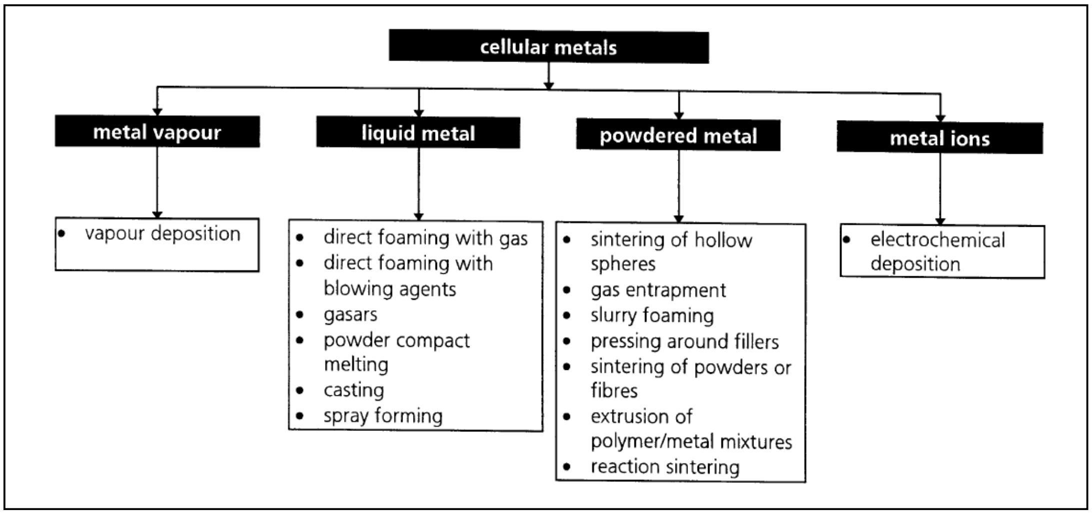

Figure 2.8: Overview of the various fabrication processes of Metal foams (Banhart, 2001)

There are various fabrication method that involved in liquid sate route categorize. The basic of the fabrication of metal foams is by direct foaming of melts. That is impossible to directly injecting gas into the liquid in order to produce metallic melts of foams. This is because, the high density of the liquid, the buoyancy forces are high, and the gas bubbles that formed to the metallic melt will be influence to the collapse of the foams. This problem can be solved by increase the viscosity of the molten metal, modifying the surface energy of the liquid limit and etc. Investment casting is also the method that can be categorized in liquid state route. In investment casting, a thermo-physical shock treatment also known as reticulation is applied to the polymeric foam. Basically, the material that used as start material is Polyurethane foam (Dukhan, 2013).

The Syntactic foams can be produced by melt filtration which these foams consist of a metallic matrix that attaches light weight elements. Usually, hollow spheres are used which can be made of Glass, Ceramic, Fly Ash or Metal and includes homogenous on it and generated closed pore structure. High pressure die casting process also the method for the production of foams or sponges by comprises the infiltration of Aluminum, Magnesium, Or Zinc melts into Polymer structures. There are three types of fabricated metal foams by melting of foamable precursors which are precursors produced by powder metallurgical methods, precursor processing in the semi-solid state, and precursor fabrication from the liquid state (Dukhan, 2013).

Nowadays, there is fabrication that no liquid metal involved, in other words the fabrication of metal foams via solid state route. The first method to produce open porous foams is using space holders. The suitable space holder must be select to make sure this space holder will be easily removed later by thermal decomposition. Next, the slurry foaming techniques is widely used in order to produce metal foams. This method involves metal powders and a suitable carrier fluid which can be described as solvent and polymeric binder. The syntactic foams that made via powder metallurgy techniques are required for materials with a high melting point like steels which melt infiltration cannot be carried (Dukhan, 2013).

In this study, the fabrication of metal foams that involved is by solid state route. The metal foams will be produce via powder metallurgy techniques which involved sintering and dissolution process in order to synthesize Stainless Steel metal foams and physical properties of the foam after sintering process.

2.5.2 Fabrication Foams using Slurry Foaming Techniques

Slurry foaming technique can be described by preparing slurry which the contents is involved, metal powders, blowing agents and some reactive additives. The next process is to pour the slurry into mould after mixing process and left at elevated temperatures. The additive and the blowing agent influence the slurry turns viscous and starts to expand as gas. When the slurry can be considered as in stable condition, the slurry need to dry completely and the sintering process will be begin. The sintering process done for produce final product of metal foams with ideal strength.

Usually, slurries foaming techniques has be done in order to produce open porous metal foams. As the example, the open porous polymer foam is dipped into a slurry that containing a mixture of Silver and Silver Oxide powder. The foams is coated and heated up to certain temperature, and make the Polymer inside the slurry will be burn out and densify the metal powder particles to produced net-shaped parts and start the sintering process and forming a rigid cellular metal structure.

There are previous researchers study the fabrication of metallic foam via slurry method route obtains the result of density of foams down to 7% have been achieved but there are problems with low strength and cracks in the foamed material (Banhart, 1971). Zhou *et al*. in his research to fabricate Stainless Steels foam was use slurry method to produce the metal foams with the additive of Polyurethane sponge and high-purity Argon to the Stainless Steel powder (Zhou *et al.,* 2008). The morphology analysis of the Stainless Steels foams is show in Figure 2.9.

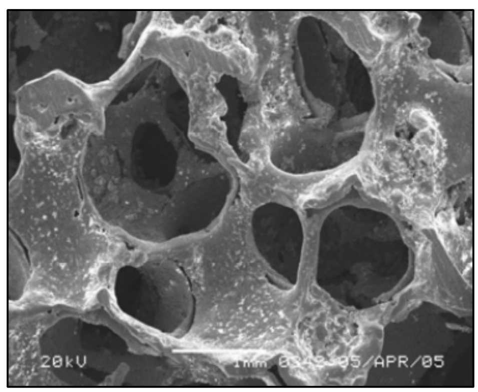

Figure 2.9: Scanning Electron Morphology (SEM) analysis of Stainless Steels foams via Slurry Method (Zhou *et al.,* 2008)

Ahmad *et al*. proposed that slurry foaming techniques in order to produce Titanium foam with addition of PEG and CMC as binder and space holder respectively. Polyurethane (PU) has been used as a scaffold. In the study also has mention that slurry foaming technique can produce open celled and high porosity of Titanium foam (Ahmad *et al*., 2010).

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